TRANSLATION

Union of Soviet Socialist Republics

Invention Specification
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255269

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Filing Date: November 1, 1968

Registration No.: 1282730/23-4

Disclosure Date: October 28, 1969, Bulletin No. 33

Specification Published: March 30, 1970

Inventors: M. I. Kabachnik, N. N. Godovikov, V. V. Pisarenko and L. S. Zakharov

Applicant: Institute of Organometallic Compounds of the USSR Academy of Sciences

Method for Preparation of Mixed Aryl Polyfluoroalkyl Phosphates

Known methods for producing mixed aryl polyfluoroalkyl phosphates are based on reaction of phosphorus oxychloride with polyfluorinated alcohols and phenols in the presence of hydrogen chloride acceptors, pyridine, alkali solution.

When aryl chlorophosphates react with alcoholates of polyfluoroalcohols, mixtures of phosphates that are difficult to separate are formed. It has not been possible to produce aryl polyfluoroalkyl phosphates by reaction of aryl chlorophosphates with polyfluorinated alcohols without hydrogen chloride acceptors.

To simplify the process, increase the yield and improve product quality it is proposed that aryl dichlorophospate or diaryl chlorophosphate be used as phosphoric acid chloride and the

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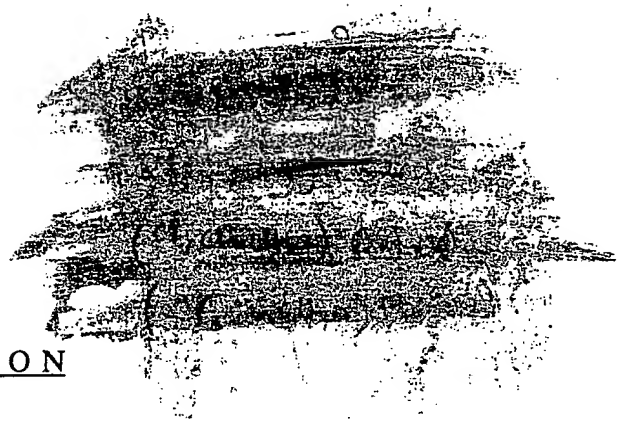

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When aryl chlorophosphates react with alcoholates of polyfluoroalcohols, mixtures of phosphates that are difficult to separate are formed. It has not been possible to produce aryl polyfluoroalkyl phosphates by reaction of aryl chlorophosphates with polyfluorinated alcohols without hydrogen chloride acceptors.

To simplify the process, increase the yield and improve product quality it is proposed that aryl dichlorophospate or diaryl chlorophosphate be used as phosphoric acid chloride and the

process be run during heating in the presence of catalytic amounts of group II metals or their salts. The reaction is run at a temperature of 90-165°C.

Mixed aryl polyfluoroalkyl phosphates can be used as plasticizers, nonflammable lubricants and additives, nonflammable hydraulic fluids.

Example 1. Phenyl-bis(1,1-dihydroperfluorobutyl) phosphate

0.025 mol phenyl dichlorophosphate and 0.06 mol 1,1-dihydroperflorobutyl alcohol are heated under reflux in the presence of 0.002 mol magnesium at 135-45°C (bath temperature) to cessation of hydrogen chloride liberation (3 hours). The temperature of the reaction mixture gradually rises to 135°C. The mixture is then held for 30 minutes under the vacuum of a water jet pump and distilled.

Phenyl-bis(1,1-dihydroperfluorobutyl) phosphate is obtained with bp 113-114°C/22 mmHg (according to literature data bp 93-96°C/1 mmHg); n_D^{20} 1.3722; d_4^{20} 1.5745; yield 86%.

Found, %: C 31.3: H 1.8: P 5.8
$C_{14}H_9F_{14}O_4P$
Calculated, %: C 31.3: H 1.7: P 5.8

Example 2. Phenyl-bis(3,3,3-trifluoropropyl) phosphate

0.025 mol phenyl dichlorophosphate is added to 0.002 mol magnesium and then 0.06 mol trifluoropropyl alcohol. Liberation of hydrogen chloride begins immediately and the temperature begins to rise slowly. After 30 minutes the temperature in the bath is raised to 135-145°C, during which the temperature of the reaction mixture increased to 124-126°C. It is held at this temperature for 0.5-1 hour and hydrogen chloride residues are eliminated along with unreacted alcohol in the vacuum of a water jet pump. By distillation phenyl bis(3,3,3-trifluoropropyl) phosphate is obtained with bp 113-114°C/1.5 mmHg; n_D^{20} 1.4234; d_4^{20} 1.3886. Yield 70%.

Found, %: C 39.7: H 3.6: P 8.3: F 31.2.
$C_{12}H_{13}F_6O_4P$
Calculated, %: C 39.4: H 3.6: P 8.5: F 31.1

Example 3. Diphenyl-(1,1-dihydroperfluorobutyl) phosphate

0.05 mol diphenyl chlorophosphate and 0.06 mol 1,1-dihydroperfluorobutyl alcohol are poured into a flask heated to 130°C with 0.002 mol magnesium and heated to cessation of hydrogen chloride liberation (5 hours), gradually raising the bath temperature to 175°C. The temperature of the reaction mixture rises to 165°C. By vacuum distillation 87% diphenyl-(1,1--dihydroperfluorobutyl) phosphate is obtained with bp 140-141°C/1.5 mmHg, according to literature data bp 127-130°C/1 mmHg; n_D^{20} 1.4539; d_4^{20} 1.4206.

Found, %: C 44.4; H 2.8; P 7.2; F 30.7
$C_{15}H_{12}F_7O_4P$
Calculated, %: C 44.5; H 2.8; P 7.2; F 30.8

Example 4. Diphenyl-(3,3,3-trifluoropropyl) phosphate

0.05 mol diphenyl chlorophosphate, 0.05 mol trifluoropropyl alcohol and 0.002 mol magnesium are slowly heated to 135-145°C (bath temperature, violent liberation of hydrogen chloride begins at a temperature of the reaction mixture of 90°C) and held at this temperature for 1.5 hours. By vacuum distillation 71% diphenyl-(3,3,3-trifluoropropyl) phosphate is obtained with bp 150-151°C/2 mmHg; n_D^{20} 1.4948; d_4^{20} 1.3025.

Found, %: C 52.4; H 4.2; P 8.9; F 16.4
$C_{15}H_{14}F_3O_4P$
Calculated, %: C 52.0; H 4.1; P 8.9; F 16.5

Claims

1. Method for preparation of mixed aryl polyfluoroalkyl phosphates by reaction of polyfluorinated alcohols with phosphoric acid chlorides, characterized by the fact that, in order to simplify the process, increase the yield and improve product quality, aryl dichlorophosphate or diaryl chlorophosphate is used as phosphoric acid chloride and the process is run during heating in the presence of catalytic amounts of group II metals or their salts.

2. Method according to Claim 1, characterized by the fact that the process is run at a temperature of 90-165°C.

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